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MOTIONAL CORRELATION TIME OF DILUTE 111CD IMPURITIES IN SE-RICH--ETC(U)
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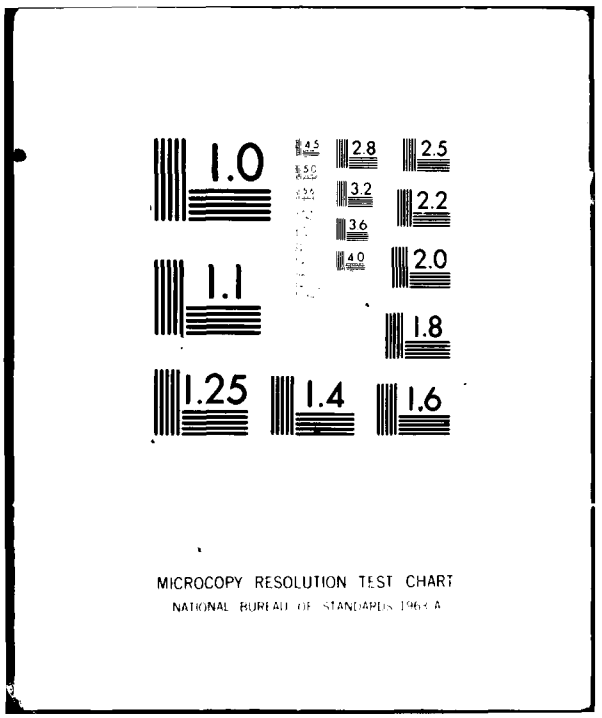
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by

D. K. Gaskill, J. A. Gardner, K. S. Krane,

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MOTIONAL CORRELATION TIME OF DILUTE ^{111}Cd IMPURITIES IN Se-RICH LIQUID Se-Te ALLOYS

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ABSTRACT

The motional correlation time, τ_c, in liquid Se and Se-rich Se-Te alloys has been investigated between 500 and 900°C using time differential perturbed angular correlations of γ-rays from dilute ^{111}Cd impurities. In all alloys we find $\tau_c \propto \exp(E_0/kT)$ at low T where $E_0 = 0.36$ eV. τ_c deviates from this relation at high T. At low T, τ_c is tentatively identified as the lifetime of a Cd to host molecule bond, and at high T as the average lifetime of bonds in the host molecule.

INTRODUCTION

The Perturbed Angular Correlation (PAC) experimental technique is not really a resonance method, but because it is a measurement of interactions between nuclei and their environment, it is informative to include it in this symposium. Physical information from PAC experiments is quite similar to that obtained from Mössbauer, NMR, and ESR hyperfine measurements.

PAC utilizes a radioactive isotope which decays via a 2-step gamma-ray cascade. The experimental work reported in this paper utilizes the isotope ^{111}In, which decays to ^{111}Cd* by electron capture. The ^{111}Cd* subsequently decays by a 171 keV gamma ray (γ_1) to an intermediate ^{111}Cd state with lifetime $\tau_N = 121$ nsec, which then decays to the ^{111}Cd ground state by emission of a 245 keV gamma (γ_2). In the absence of magnetic fields or electric field gradients at the Cd nucleus, γ_2 would be emitted with an anisotropic probability proportional to

$$W(\theta) = [1 + A_2P_2(\cos\theta) + A_4P_4(\cos\theta)] \qquad (1)$$

where θ is the angle of emission of γ_2 with respect to the direction of γ_1, and the nuclear angular correlation constants are given by $A_2 = -0.180$, $A_4 = 0.002$, for this cascade. In general, however, a Cd nucleus in condensed matter will be subject to magnetic and/or electric fields due to nearby electrons and ions. Thus the nucleus will be subjected to torque during the time between emission of γ_1 and γ_2, so in general the angular distribution of Eq. 1 must be modified to include the effects of reorientation of the nuclear ensemble by interaction with these fields. For a polytropic sample (i.e., one with no preferred overall orientation such as a liquid or powder) then

$$W(\theta,t) = [1 + A_2G_2(t)P_2(\cos\theta) + A_4G_4(t)P_4(\cos\theta)] \qquad (2)$$

The functions $G_2(t)$ and $G_4(t)$ are normalized to unity at $t = 0$ and are governed by the hyperfine interactions. The purpose of a PAC experiment is to measure G_2 and G_4 and relate them to the electronic properties of the material being investigated. Because in our case A_4 is quite small, the last term in Eq. 2 contributes negligibly to $W(\theta,t)$, and we shall drop it. It is easy to show [1] that $G_2(t)$ can be determined experimentally by measuring $W(\theta,t)$ at $\theta = 90^o$ and 180^o. Then

$$A_2G_2(t) = 2\,\frac{W(180^o,t) - W(90^o,t)}{W(180^o,t) + 2W(90^o,t)} \quad . \qquad (3)$$

Normally, it is possible to measure $W(\theta,t)$ between $t = 0$ and several times τ_N. Details of the experimental procedure for measuring $W(\theta,t)$ are given elsewhere. [2,3]

USE OF PAC TO STUDY ELECTRONIC PROPERTIES OF LIQUIDS

Both magnetic fields interacting with the nuclear magnetic moment and electric field gradients interacting with the nuclear quadrupolar moment can perturb the nucleus significantly in its intermediate state, but the latter is dominant in this experimental work, so we shall ignore magnetic fields in this discussion. We shall also discuss only the situation for which electric field gradients in the liquid fluctuate rapidly with respect to τ_N. For such a situation, it has been shown [4] that G_2 should decrease exponentially with time as

$$G_2(t) = e^{-\lambda t} \qquad (4)$$

where

$$\lambda = 2.487\,\tau_c\langle\nu_Q^2\rangle \quad . \qquad (5)$$

Here $\langle\nu_Q^2\rangle$ is the average square quadrupolar interaction frequency and τ_c is the correlation time of electric field gradient fluctuations. The fluctuations can be caused either by physical tumbling of the molecule to which the nucleus is bound or by electronic processes which cause the chemical bonding to change rapidly. In either case τ_c is a quantity of physical interest, but in the present experiments we have investigated a class of liquids in which τ_c is expected to be dominated by chemical fluctuations. $\langle\nu_Q^2\rangle$ can be roughly estimated for these liquids and should not depend strongly on temperature. Thus our PAC measurements provide a semi-quantitative value for τ_c and a relatively accurate measure of its temperature dependence. This information on chemical kinetics is of considerable interest and is not often measureable by other means.

EXPERIMENTAL RESULTS AND DISCUSSION

The work reported here on Se-rich liquid Se-Te alloys is an extension (to materials expected to have more rapid chemical bonding fluctuations) of PAC measurements on liquid Se. [2,3] For pure Se, τ_c varies from approximately 20 psec at 900°C to 200 psec at 500°C. Over most of the range τ_c varies with temperature as

$$\tau_c \propto e^{E_o/kT} \qquad (6)$$

where E_0 = 0.36 eV, but the data deviate significantly from this relation above 800°C. We find qualitatively similar behavior in the Se-Te alloys. The log of experimentally determined values of λ are shown vs T^{-1} in Fig. 1. In this figure, the right-hand ordinate shows the value of τ_c obtained from λ using Eq. 5 and $\langle\nu_Q^2\rangle^{1/2}$ = 125 MHz. [2] In Fig. 2 we show τ_c for pure Se on a compressed scale and include low temperature correlation times obtained recently by Warren and Dupree [5] from ^{77}Se NMR line-broadening chemical-shift anisotropy in pure liquid Se.

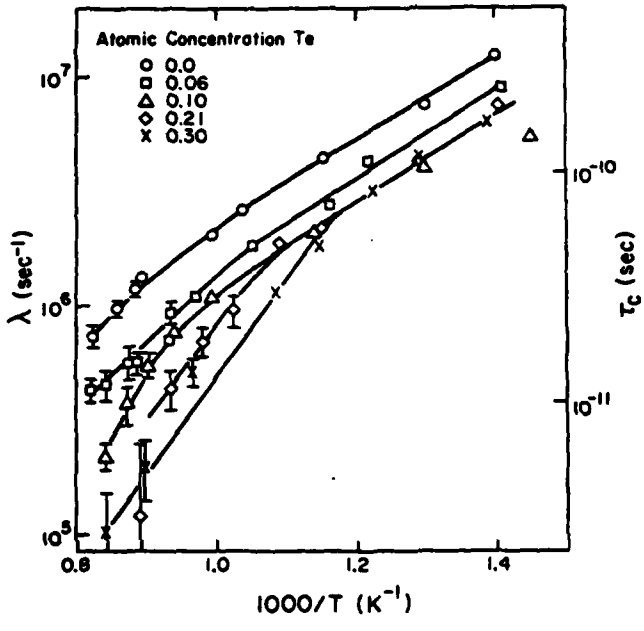

Fig. 1: Log λ vs T^{-1} for Cd in liquid Se-Te alloys. The right hand ordinate shows τ_c if $\langle\nu_Q^2\rangle^{1/2}$ = 125 MHz. The straight lines through the points at low T have slope E_0 = 0.36 eV. The curves through the points at high temp are only a guide to the eye.

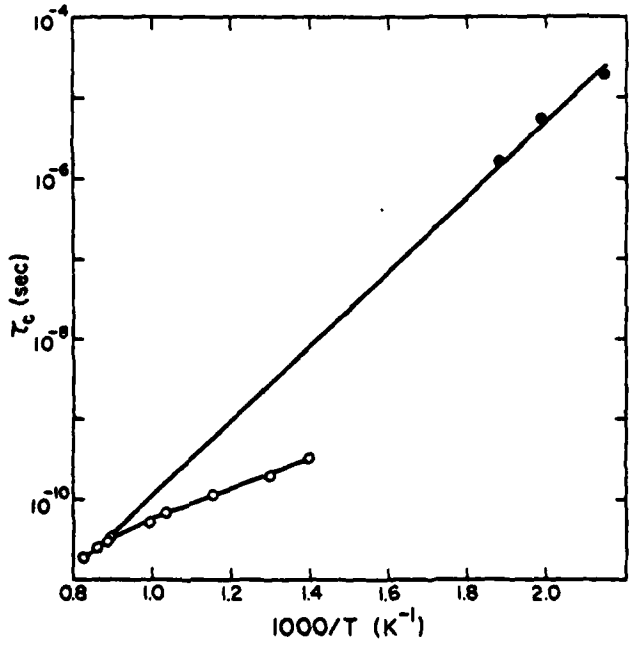

Fig. 2: Log τ_c vs T^{-1} in liquid Se. The solid points are intrinsic correlation times measured by NMR [Ref. 5]. Open points are for Cd impurities measured by PAC, assuming $\langle\nu_Q^2\rangle^{1/2}$ = 125 MHz.

Liquid Se is a weakly-bonded polymeric liquid in which the polymer size decreases with temperature due to thermal dissociation. At the highest temperatures investigated in this work, the average Se polymer size is estimated to be of order 10^2 atoms. [5,6] The Se-rich Se-Te alloys are qualitatively similar with somewhat weaker average bonding [7] so the polymer size and correlation times are expected to be somewhat smaller than for pure Se. Since electric field gradients at ^{129}I and ^{125}Te tracers are somewhat smaller in Te than in Se [8], $\langle \nu_Q^2 \rangle$ may also be slightly reduced. The correlation times measured in PAC experiments will be the minimum of the polymer rotation time, the Se-Se (or in the alloys an average Se-Se, Se-Te, and Te-Te) bond lifetime, or the lifetime of the bond between the Cd tracer and the polymer molecule. In these liquids there is probably no physical difference between the first two correlation times, since the molecules almost certainly "rotate" by breaking and reforming bonds between adjacent molecules. There is of course a very important difference between this "intrinsic" correlation time and the "tracer" correlation time due to Cd bond fluctuations, and it is important to identify which of the two is the measured quantity.

The existence of two different temperature regions for λ which is evident in Fig. 1 suggests that in one region, τ_c is intrinsic and is tracer-related in the other. This suggestion is further supported by the NMR measurements of τ_c shown in Fig. 2. The NMR correlation times are intrinsic and are consistent with an extrapolation to low temperature of the pure Se high-T region but not the low-T PAC data. The implication is that the high-T PAC correlation times are intrinsic and that the low-T correlation times are extrinsic in the sense that τ_c is dominated by Cd-polymer bond fluctuations. In principle this identification can be proven definitively by PAC measurements with other isotopes, and we are presently exploring this possibility.

It is clear from Fig. 1 that addition of small amounts of Te to Se causes an overall reduction of λ. Since the activation energy in the low-T "extrinsic" region is unchanged by adding Te, it is possible that at low T the change may be due to reduction of $\langle \nu_Q^2 \rangle$, and that τ_c is not affected by alloying. This possibility can be checked by PAC measurements at sufficiently low temperature that $\tau_c \gg \tau_N$, $(\langle \nu_Q^2 \rangle)^{-\frac{1}{2}}$ where $G_2(t)$ becomes independent of τ_c, and $\langle \nu_Q^2 \rangle$ can be determined directly. Although we are unlikely to achieve this condition in the liquid state, the corresponding quenched glass should be an adequate substitute. Unfortunately, our preliminary measurements at lower temperatures have been inconclusive because of experimental difficulties in sample preparation.

The PAC data in the interesting high-T region are relatively inaccurate because the decay of $G_2(t)$ is very small within the experimentally accessible time range. Nonetheless it is clear that the relative decrease of λ with addition of Te is greater than in the low-T region. Although part of this decrease may be ascribed to change of $\langle \nu_Q^2 \rangle$, τ_c must also be decreased by addition of Te. This is in accord with naive expectations, since adding Te is known to weaken the bonding. The "intrinsic" τ_c temperature dependence cannot be determined with confidence from the present data. If τ_c is activated in this region, the activation energy is of order 0.9 eV for the higher Te-content alloys, approximately the same as the slope of the line which connects the low and high-T "intrinsic" pure Se correlation times in Fig. 2

More accurate data in this region are required before one can draw any reliable conclusions about the temperature dependence of τ_c in this region however.

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